Separating Thermal, Electronic, and Topographic Effects in Pulsed Laser Melting and Sputtering of Gold

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An attempt was made to separate thermal from electronic effects during laser sputtering of gold by partitioning the target surface energy between steady-state electron beam heating and pulsed laser heating. For flat starting surfaces and a peak surface temperature of ~2700 K, the Au translational energy remains $(2-3)\times$ higher than classical expectations and is insensitive to how energy is partitioned between steady-state heating and laser heating. The mean desorption energy is linearly dependent on peak surface temperature, but with a slope of $15k_BT$ as opposed to the classical $2k_BT$.

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The thermal nature of pulsed laser sputtering of metals (below the plasma onset) has been questioned by relatively few researchers. The wisdom of a thermal description [1] is supported by the conventional picture of how metals absorb and dissipate radiative energy. Photons are absorbed almost exclusively by conduction band electrons, while electron-phonon energy relaxation occurs on a time scale of ~1 ps. Therefore, with nanosecond- or longer-duration laser pulses, it seems reasonable to expect that the metal surface (solid or liquid) will remain in local thermodynamic equilibrium and that particles will leave the surface by classical sublimation or evaporation. In this case, the translational energy flux distribution of the emitted particles should have the Maxwell-Boltzmann form

$$P(E) \sim E \exp(-E/k_BT_s), \quad (1)$$

where $\overline{E} = 2k_BT_s$ is the mean translation energy and T_s is the surface temperature [2]. A good example of agreement between experiment and thermal expectations is given in a recent study by Gibert and Dubreuil [3] on laser-irradiated Fe.

Standing apart from such thermal expectations is a large body of work [4] on DIET processes (desorption induced by electronic transitions). A prerequisite for DIET is some mechanism of localizing electronic energy on one lattice site for times sufficiently long to lead to energetic particle emission. For low photon energies (less than about 6 eV), most DIET literature is concerned with semiconductors and dielectrics, where the band gap (and defect states localized within the gap) provides plausible scenarios for creating energetic particles through hole localization and electron-hole recombination processes.

Surprisingly, a number of recent studies suggest that electronic excitations may also be involved in desorption processes from metals at low photon energies. Hoheisel, Vollmer, and Träger [5] have shown that metal atoms can be desorbed from small metal clusters by low-power cw laser radiation. The dependence on wavelength, power and cluster size clearly indicates that collective surface plasmon excitations play a role in stimulating the desorption. However, as these authors correctly point out, it is not obvious why a collective excitation of the conduction electrons over the whole surface of a cluster should lead to energetic particle emission. Other researchers have invoked surface plasmons to rationalize the production of energetic neutrals and ions from continuous metal films using nanosecond-duration laser pulses at fluences below the melting threshold. Lee, Callcott, and Arakawa [6] reported bimodal energy distributions of gold atoms desorbed from a continuous film with 532 nm laser pulses ($\tau = 7$ ns). The gold film was coated on a glass prism, and total internal reflection (TIR) at the glass-film interface was used to enhance surface plasmon excitation via the evanescent wave. Lee, Callcott, and Arakawa argued that their high-energy gold peak (~0.3 eV) was due to an electronic de-excitation process involving surface plasmons. Kim and Helvajian [7] observed similarly energetic desorption of Ag^+ ions (~0.7 eV) from continuous silver films using both a TIR geometry and direct irradiation from the vacuum side. They argued that the film roughness must have been sufficient to support surface plasmon excitation at the metal-vacuum interface. Shea and Compton [8] also invoked surface plasmons to explain high energy (3.6 eV) Ag^+ ions ejected from a rough (ablated and redeposited) silver surface by 30 ps laser pulses. Some theoretical work [9] has been attempted to justify the plasmon interpretation of experimental results.

In an earlier study from this laboratory [10], KrF laser sputtering of gold was studied at fluences sufficient for surface melting, but vaporizing at most a few monolayers of gold atoms per pulse. Atoms were observed to leave the surface with almost perfect Boltzmann translational energy distributions, but the energies were far too high to reconcile with a thermal model. Quantitative analysis of these results was not possible because of rapid hydrodynamic development of high-aspect-ratio surface structures (ridges and droplets) with dimensions comparable to the thermal diffusion length. This destroys the simple picture of a homogeneous surface temperature.

The question arises: Would the system behave thermally if the surface remained flat during the measurement? We attempt to answer this question by studying laser sputtering from well-characterized surfaces, using small numbers of laser pulses to minimize the changes in surface topography. We also compare results at the same peak surface temperature while the partitioning of energy between steady-state heating and pulsed laser heating is varied. Quantitative one-dimensional heat transfer calculations are used to fix the temperature scale and assess departures from the thermal model.

KrF excimer laser pulses ($\lambda = 248$ nm, $\tau = 16$ ns) were delivered to the polycrystalline gold target (25 mm diameter $\times$ 1.5 mm thick, 99.999% purity) using a beam delivery system described previously [10]. In the present work a doublet lens was used to reimage the light tunnel exit plane at $-0.22\times$ magnification, producing a 0.7 mm square spot with a top-hat intensity distribution for normal incidence. The target was mounted in a large vacuum chamber, viewed by a differentially pumped mass spectrometer [11]. Neutral gold atom time-of-flight (TOF) distributions were measured and converted to translational energy flux distributions, $P(E)$, in the usual way. The steady-state temperature of the target was controlled by electron-beam heating from the back side, holding the target at +100 V with respect to the filament. A thermocouple was used to monitor the target temperature.

One of the technical challenges of this study was obtaining well-defined surfaces from which to make measurements on the very first laser pulses. The most obvious approach of using a mechanically polished surface proved unsatisfactory due to signal interference from contaminants buried in the selvedge region. An aggressive etch in aqua regia (3:1 HCl/HNO_3) provides an extremely clean surface (as verified by x-ray photoelectron spectroscopy). The high-frequency roughness of the as-etched surface [shown in Fig. 1(a)] was removed by preconditioning the surface with the laser prior to taking data. The target was in vacuum during this process and received about 30 laser pulses per unit area at 0.55 J/cm^2 over a 15 mm $\times$ 15 mm serpentine scan area. Preconditioning involves some compromise in control over local topography development. The problem is minimized if the target is irradiated while held at high temperature (1100 K) because of the resulting low periodicity of hydrodynamic topography growth. A typical result of laser preconditioning is shown in Fig. 1(b). Note that the height scale is greatly exaggerated; the maximum surface slope is only 3–4°. This is small enough to make local geometrical fluence enhancements unimportant, and the heat transfer problem remains one dimensional. For TOF measurements, the target was rotated so that the surface normal lay parallel to the detector axis ($\vartheta_{\text{det}} = 0°$). This makes the angle of incidence 45°. Unless noted otherwise, the preconditioned target surface was used for all measurements presented below.

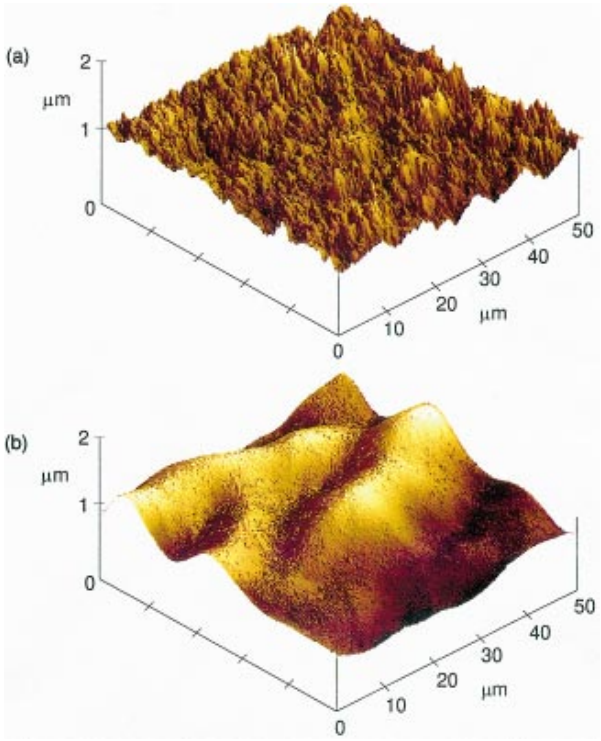

FIG. 1 (color). (a) AFM image of gold surface after etching in aqua regia. (b) Same surface after laser preconditioning at high temperature ($T_0 = 1100$ K, $\phi = 0.55$ J/cm^2, $N = 30$ pulses). Note that the height scale is exaggerated by more than $10\times$ relative to the scale of the x and y axes in both images. The maximum slope on the smoothed surface is only 3–4°.

The data shown in Fig. 2 was obtained using six different static target temperatures T_0, with the fluence adjusted in each case to keep the peak calculated surface temperature T_{peak} as close as possible to 2700 K [12]. The fraction of surface heating provided by the laser varies from 59% at $T_0 = 1100$ K to 87% at $T_0 = 350$ K. At each value of T_0, data were taken at 18 spots. At each spot, five 10-shot TOF measurements were recorded sequentially, creating bins for laser pulses $N = 1{-}10, 11{-}20, \ldots, 41{-}50$. A total of 540 TOF distributions were analyzed to obtain yield and translational energy data.

Consider first the data from the initial two TOF bins (open circles and squares in Fig. 2), which are least affected by changes in surface topography. Three intriguing results emerge. First, the measured mean translational energies of ~1.3 eV are much higher than the predicted $\overline{E} = 2k_B T_{\text{peak}} = 2k_B(2700) = 0.46$ eV from classical evaporation theory. Second, both the yield and desorption energy show little if any dependence on how energy is partitioned between pulsed laser heating and steady-state heating. This result is surprising since we would expect this system to approach the classical $2k_BT$ result in the limit that fluence goes to zero. Third, even though the mean desorption energies are hyperthermal, the experimental $P(E)$'s are remarkably faithful to the Maxwell-Boltzmann *shape* (see Fig. 3).

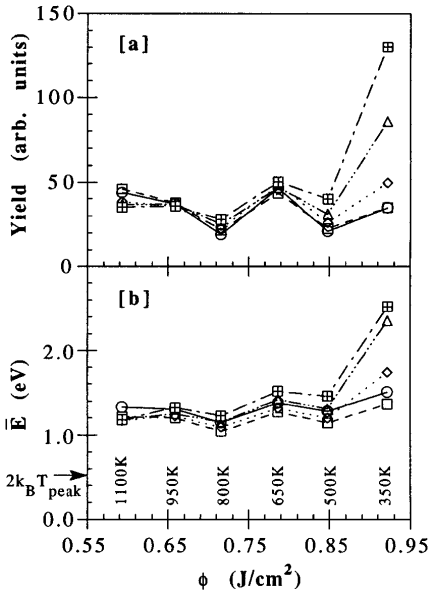

FIG. 2. (a) Average yields and (b) mean translational energies of Au atoms for six different combinations of fluence and static target temperature, the pairs chosen to create the same *peak* surface temperature of ~2700 K. Symbols correspond to different cumulative numbers of laser pulses on the preconditioned surface: (○) $N = 1-10$, (□) $N = 11-20$, (◇) $N = 21-30$, (△) $N = 31-40$, and (⊞) $N = 41-50$.

If one now looks at the data points in Fig. 2 corresponding to larger accumulated numbers of laser pulses, the effects of topography development can be seen. At the lower static target temperatures, and 350 K in particular, both energies and yields increase after the first 20 laser pulses due to local fluence enhancement from developing high-aspect-ratio surface topography. However, at high static temperatures the surface remains flatter through greater number of laser pulses because of the longer periodicity of surface structures. Consequently, at higher static target temperatures, the data points for all five TOF bins remain close together.

Figure 4 summarizes the results of another experiment in which the peak surface temperature was varied. Three fluence values were explored at each of two static target temperatures. The mean translational energy for the $N = 1-10$ shot bin is plotted against the peak calculated surface temperature. Figure 4 demonstrates that the slope of energy with respect to temperature is approximately $15k_B$, as opposed to $2k_B$ predicted by theory.

Our results demonstrate substantial discrepancies between the desorption energy and surface temperature, raising the question of our confidence level in the calculated temperatures. There are essentially three categories of uncertainties for the calculation: thermal properties, equilibrium assumptions, and optical properties. Equilibrium temperature-dependent thermal properties for both the liquid and solid phases are readily available and are taken at face value [12]. Our study uses 16 ns pulses which is vastly longer than the time scale for electron-phonon thermalization in metals, justifying the assumption of local quasiequilibrium. The final issue of the optical properties will be commented on in the following paragraph. Our confidence level for the absolute temperature scale is about 20%. We base this on a study in which we experimentally found the threshold for surface melting and compared that with our numerical calculations. Our uncertainty in predicting relative changes in surface temperature (which is all that matters for the energy partitioning experiment, for example) is less than 10%.

For smooth surfaces, the optical properties are well known and believed to be insensitive to temperature.

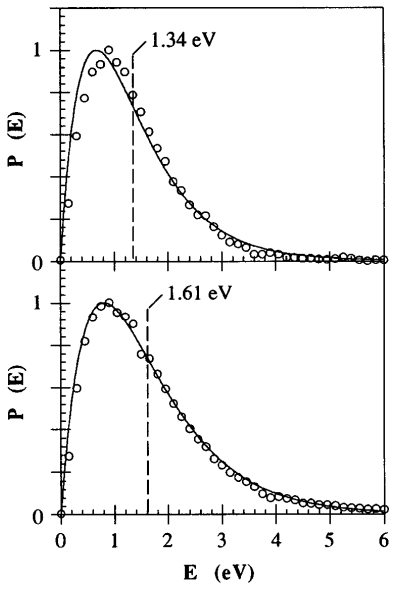

FIG. 3. Translational energy distributions for the two extreme static temperature and fluence pairs of Fig. 2. The circles represent a direct inversion of the experimental TOF distributions for the $N = 1-10$ shot bin. The solid curves are Boltzmann distributions having the same mean energies (indicated by dashed lines) as the experimental distributions.

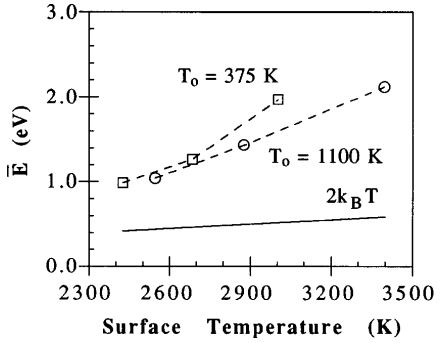

FIG. 4. Mean translational energy of Au atoms vs peak calculated surface temperature for the first 10 laser pulses on a preconditioned surface. Data for two different static target temperatures are shown.

However, surface asperities may have a nonlinear effect on the coupling of laser light to the surface. This is the foundation for the surface plasmon excitation picture, and the principle motivation for the preconditioning procedure that removes high-frequency surface structures through melting. Nevertheless, no conceivable change in optical constants (nonlinear effects included) could elevate the surface temperature by a factor of 2–3. The 248 nm reflectivity of Au at 45° incidence is 26% for our predominantly p-polarized light. So even if *all* the incident light were to be absorbed, that would give only a 35% increase in surface temperature.

The final data to be reported here concern the change in the gold atom translational energy during the 30-shot high-temperature preconditioning procedure. The experiment was performed on discrete spots at $\vartheta_{\text{inc}} = 45°$. Ten sequential 3-shot TOF measurements were recorded at each spot, and the binned results were co-added and inverted to give the mean translational energies. The rough initial surface of Fig. 1(a) produces a mean translation energy over 5 eV ($T_0 = 1100$ K, $\phi = 0.55$ J/cm^2). The translational energy asymptotically approaches a value slightly above 1 eV for the final smoother surface of Fig. 1(b). The factor of 4–5 rolloff in desorption energy is clearly beyond explanations revolving on changes in net energy coupling to the surface due to roughness. Yet the shape of the $P(E)$ remains close to Boltzmann in all cases.

These results demand a reevaluation and refinement of our ideas concerning thermal, electronic, and topographic effects in laser sputtering of metals. In contrast to other reports in the literature, we have never observed a thermal energy distribution, nor have we observed a bimodal energy distribution with a "slow" thermal component and a "fast" electronic or DIET component. Indeed, the behavior we observe does not fall cleanly into the thermal or DIET camps, but is some sort of hybrid between the two. Even for flat smooth surfaces, where plasmon excitation should be very inefficient, the mean Au translational energy is (2–3)× higher than classical evaporation theory predicts. When the target surface is microscopically rough, the Au yields and translational energies are greatly enhanced. This last point is qualitatively consistent with plasmon involvement, but our $P(E)$'s prove that some atoms are directly ejected with translational energies greater than either the quantized plasmon energy or the photon energy. The real situation appears to be more complex than the picture put forward by Ritchie, Manson, and Echenique [9] (i.e., a single quantized surface plasmon transferring most of its energy to a single ion or atom with momentum conservation provided by the lattice). Perhaps the most remarkable result or our study is that, over the entire range of conditions explored, the gold atom $P(E)$ remains faithful to the Maxwell-Boltzmann form, and the mean desorption energy tracks with the surface thermal condition, despite the energies being hyperthermal. These facts may hold the clue to better theoretical understanding.

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[12] The numerical calculation uses the enthalpy method described in [10], with the sole change that the surface boundary condition is now prescribed by a kinetic relation between surface temperature and vapor flux. The thermal and optical constants of gold are summarized in Table I of [10], and references cited therein.